

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 July 2004 (15.07.2004)

PCT

(10) International Publication Number
WO 2004/058876 A1

(51) International Patent Classification⁷: C08L 23/04,
C08F 297/08

Rainer [DE/DE]; Augustaanlage 26, 68165 Mannheim
(DE).

(21) International Application Number:
PCT/EP2003/013867

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 6 December 2003 (06.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
102 61 066.5 24 December 2002 (24.12.2002) DE
60/445,163 5 February 2003 (05.02.2003) US

(84) Designated States (regional): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for all designated States except US): BASELL
POLYOLEFINE GMBH [DE/DE]; Brühler Strasse,
50389 Wesseling (DE).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/058876 A1

(54) Title: POLYETHYLENE BLOW MOULDING COMPOSITION FOR PRODUCING JERRY CANS

(57) Abstract: The invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for the blow moulding of canisters having a volume in the range of from 2 to 20 dm³ (I). The composition has a density in the range from 0.950 to 0.958 g/cm³ at 23 °C and an MFR_{190/5} in the range of from 0.30 to 0.50 dg/min. It comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.

Title: Polyethylene blow moulding composition for producing jerry cans

The present invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for blow moulding of
5 canisters with a capacity in the range from 2 to 20 dm³ (l) (jerry cans), and to a process for preparing this polyethylene composition in the presence of a catalytic system composed of a Ziegler catalyst and a co-catalyst, by way of a multistage reaction process composed of successive slurry polymerizations.
10 The invention further relates to the canisters produced from the molding composition by blow moulding.

Polyethylene is widely used for producing blow mouldings of all types requiring a material with particularly high mechanical strength, high corrosion resistance, and absolutely reliable long-term stability. Another particular advantage of
15 polyethylene is that it also has good chemical resistance and is intrinsically a lightweight material.

EP-A-603,935 has previously described a blow moulding composition based on polyethylene having a bimodal molecular mass distribution, which is suitable for
20 the production of mouldings with good mechanical properties.

US-A 5,338,589 describes a material with even broader molecular mass distribution, prepared using a high-mileage catalyst known from WO 91/18934, in which the magnesium alcholate is used in the form of a gel-like suspension.
25 Surprisingly, it has been found that the use of this material in mouldings, in particular in pipes, permits simultaneous improvement in properties which are usually contrary correlated in semicrystalline thermoplastics, these being stiffness and creep on the one hand and stress-crack resistance and toughness on the other hand.

However, the known bimodal products in particular have relatively low melt strength during processing. This means that the extruded parison frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being 5 produced, the wall thickness is found to be non-uniform, due to flow of the melt from upper regions into lower regions.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow moulding which can give a further improvement over all of 10 the known materials in processing by blow moulding to canisters. In particular, the high melt strength of the moulding composition permits to run an extrusion process without parison disruption over a long time period, and the precisely adjusted swell ratio index of the composition permits optimization of wall-thickness control.

15 We have found that this objective is achieved by a composition as mentioned at the outset, the characterizing features of which are that it comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and 20 from another 1-olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene-1-olefin copolymer C, where all of the percentage data are based on the total weight of the composition.

25 The invention also relates to a process for preparing this composition in a cascaded slurry polymerization and to a process for producing, from this composition, canisters with a capacity in the range from 2 to 20 dm³ (l) and with quite excellent mechanical strength properties.

30 The polyethylene composition of the invention has a density in the range from 0.950 to 0.958 g/cm³ at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small

proportions of other olefin monomer units having from 4 to 8 carbon atoms, namely from 0.2 to 0.5 % by weight. Examples of these comonomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene homo- or copolymer C also contains an 5 amount in the range from 1 to 2 % by weight of one or more of the above mentioned comonomers.

The composition of the invention has a melt flow index ISO 1133 in the range of from 0.30 to 0.50 dg/min, expressed in terms of $MFR_{190/5}$, and a viscosity 10 number VN_{tot} in the range of from 330 to 380 cm^3/g , in particular from 340 to 370 cm^3/g , measured according to ISO/R 1191 in decalin at 135 °C.

The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of 15 the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers formed in each of the stages of the reaction are therefore as follows:

The viscosity number VN_1 measured on the polymer after the first 20 polymerization stage is identical with the viscosity number VN_A of the low-molecular-mass polyethylene A and according to the invention is in the range from 60 to 80 cm^3/g .

The viscosity number VN_2 measured on the polymer after the second 25 polymerization stage is not equal to VN_B of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be determined by calculation, but represents the viscosity number of the mixture of polymer A and polymer B. According to the invention, VN_2 is in the range from 160 to 200 cm^3/g .

The viscosity number VN_3 measured on the polymer after the third polymerization stage is not equal to VN_C of the ultra-high-molecular-mass copolymer C formed in the third polymerization stage, which can only be determined by calculation, but represents the viscosity number of the mixture of 5 polymer A, polymer B, and polymer C. According to the invention, VN_3 is in the range of from 330 to 380 cm^3/g , in particular from 350 to 370 cm^3/g .

The polyethylene is obtained by polymerizing the monomers in slurry in the range of from 70 to 90 °C, preferably from 80 to 90 °C, at a pressure in the 10 range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound such as triethylaluminum, triisobutylaluminum, alkylaluminum-chlorides or alkylaluminumhydrides. The polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being 15 regulated with the aid of hydrogen feed.

The polyethylene composition of the invention may comprise other additives alongside the polyethylene. Examples of these additives are heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds 20 which destroy peroxide, and basic costabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistats, blowing agents, or a combination of these, in total amounts of from 0 to 50 % by weight, based on the total weight of the mixture.

25

The composition of the invention is particularly suitable for the blow moulding process to produce canisters, by first plastifying the polyethylene composition in an extruder in the range from 200 to 250 °C and then extruding it through a die into a mould, where it is cooled and solidified.

30

The composition of the invention gives particularly good processing behavior in the blow moulding process to give canisters because it has a swell ratio index in the range of from 130 to 145 %, and the canisters produced therewith have particularly high mechanical strength because the moulding composition of the 5 invention has a notched impact strength (ISO) in the range from 14 to 17 kJ/m². The stress-crack resistance (FNCT) is in the range from 150 to 220 h.

The notched impact strength_{ISO} is measured according to ISO 179-1/1eA / DIN 53453 at 23 °C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is 10 inserted using an angle of 45°, with a depth of 2 mm and with a notch base radius of 0.25 mm.

The stress-crack resistance of the molding composition of the invention is determined by an internal test method and is given in h. This laboratory method 15 is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and corresponds to ISO/FDIS 16770, which has since come into force. In ethylene glycol as stress-crack-promoting medium at 80°C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced 20 by sawing out three specimens of dimensions 10 x 10 x 90 mm from a pressed plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth is 1.6 mm.

Example 1

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 1.3 Mol/h related to the titanium compound of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the 5 operative number 2.2 in the WO, was fed into the first reactor together with 2.7 Mol/h triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene, and hydrogen. The amount of ethylene (= 6.75 t/h) and the amount of hydrogen (= 7.3 kg/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas phase of the first reactor were 10 18 % by volume and 70 % by volume, respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 84 °C.

15 The slurry from the first reactor was then transferred into a second reactor, in which the percentage proportion of hydrogen in the gas phase had been reduced between 10 to 12 % by volume, and an amount of 16.6 kg/h of 1-butene was added to this reactor alongside 4.35 t/h of ethylene. The amount of hydrogen was reduced by way of intermediate H₂ depressurization. 70 % by 20 volume of ethylene, 10.5 % by volume of hydrogen, and 1.1 % by volume of 1-butene were measured in the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 82 °C.

25 The slurry from the second reactor was transferred to the third reactor using further intermediate H₂ depressurization to adjust the amount of hydrogen to 0.5 % by volume in the gas phase of the third reactor.

An amount of 67 kg/h of 1-butene was added to the third reactor alongside an amount of 3.90 t/h of ethylene. A percentage proportion of from 85 % by volume of ethylene, 0.5 % by volume of hydrogen, and 2.2 % by volume of 1-butene was measured in the gas phase of the third reactor, the rest being a 5 mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 80 °C.

The long-term polymerization catalyst activity required for the cascaded process 10 described above was provided by a specifically developed Ziegler catalyst as described in the WO mentioned at the outset. A measure of the usefulness of this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of between 1 to 8 h.

15 The diluent was removed from the polymer slurry leaving the third reactor, and the material was dried and then pelletized.

Table 1 shown below gives the viscosity numbers and quantitative proportions 20 w_A , w_B , and w_C of polymer A, B, and C for the polyethylene moulding composition prepared in Example 1.

Table 1

Example No.	1
density [g/cm ³]	0.954
MFR _{190/5} [dg/min]	0.40
w_A [% by weight]	45
w_B [% by weight]	29

W _c [% by weight]	26
VN ₁ [cm ³ /g]	70
VN ₂ [cm ³ /g]	180
VN _{tot} [cm ³ /g]	360
SR [%]	135
FNCT [h]	170
NIS _{ISO} [kJ/m ²]	16

The abbreviations for physical properties in Table 1 have the following meanings:

- 5 - SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s⁻¹, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.
- 10 - FNCT = stress-crack resistance (Full Notch Creep Test) tested using the internal test method of M. Fleißner, in [h],
- NIS_{ISO} = notched impact strength measured to ISO 179-1/1eA / DIN 53453 in [kJ/m²] at 23 °C.

We claim

5

1. A polyethylene moulding composition with multimodal molecular mass distribution, which has a density in the range of from 0.950 to 0.958 g/cm³ at 23 °C and an MFR_{190/5} in the range of from 0.30 to 0.50 dg/min, and which comprises from 40 to 50 % by weight of a low-molecular-mass ethylene homopolymer A, from 25 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 24 to 28 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the moulding composition.

15

2. A polyethylene composition as claimed in claim 1, wherein the high-molecular-mass copolymer B contains small proportions of from 0.2 to 0.5 % by weight of co-monomer having from 4 to 8 carbon atoms, based on the weight of copolymer B, and wherein the ultrahigh-molecular-mass ethylene copolymer C contains an amount in the range from 1 to 2 % by weight of comonomers, based on the weight of copolymer C.

20

3. A polyethylene composition as claimed in claim 1 or 2, which, as co-monomer, contains 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, or a mixture of these.

25

4. A polyethylene composition as claimed in one or more of claims 1 to 3, which has a viscosity number VN_{tot} of from 330 to 380 cm³/g, preferably from 340 to 370 cm³/g, measured to ISO/R 1191 in decalin at 135 °C.

30

5. A polyethylene composition as claimed in one or more of claims 1 to 4, which has a swell ratio in the range of from 130 to 145 %, and a notched impact strength (ISO) in the range of from 14 to 17 kJ/m², and a stress-crack resistance (FNCT) in the range of from 150 to 220 h.
- 10 6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in suspension at a temperature in the range of from 20 to 120 °C, at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, where the molecular mass of the polyethylene prepared in each stage is regulated with the aid of hydrogen.
- 15 7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number VN₁ of the low-molecular-mass polyethylene A is in the range from 60 to 80 cm³/g.
- 20 8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number VN₂ of the mixture of polymer A and polymer B is in the range from 160 to 200 cm³/g.
- 25 9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number VN₃ of the mixture of polymer A, polymer B, and polymer C is in the range of from 330 to 380 cm³/g, in particular of from 340 to 370 cm³/g.

10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing canisters with a capacity in the range from 2 to 20 dm³ (I), where the polyethylene composition is first plasticized in an extruder in the range from 200 to 250 °C and is then extruded through a die into a mould, where it is first blown up and then cooled and solidified.

* * * * *

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 45 980 A (ELENAC GMBH) 29 March 2001 (2001-03-29) the whole document -----	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20 August 1985 (1985-08-20) the whole document -----	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22 June 1982 (1982-06-22) the whole document -----	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5 June 2001 (2001-06-05) the whole document ----- -/-	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the International search

25 March 2004

Date of mailing of the International search report

31/03/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Golde, L

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 603 935 A (SOLVAY) 29 June 1994 (1994-06-29) cited in the application the whole document -----	1-10

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
DE 19945980	A	29-03-2001		DE 19945980 A1 AT 244264 T AU 769434 B2 AU 7001700 A BR 0014232 A CA 2387708 A1 CN 1376170 T DE 50002772 D1 WO 0123446 A1 EP 1228101 A1 JP 2003510429 T	29-03-2001 15-07-2003 29-01-2004 30-04-2001 04-06-2002 05-04-2001 23-10-2002 07-08-2003 05-04-2001 07-08-2002 18-03-2003
US 4536550	A	20-08-1985		JP 1012777 B JP 1612249 C JP 59196345 A JP 1012778 B JP 1612250 C JP 59196346 A JP 60036546 A JP 1012781 B JP 1612255 C JP 60036547 A CA 1218181 A1 DE 3470168 D1 EP 0129312 A1	02-03-1989 30-07-1991 07-11-1984 02-03-1989 30-07-1991 07-11-1984 25-02-1985 02-03-1989 30-07-1991 25-02-1985 17-02-1987 05-05-1988 27-12-1984
US 4336352	A	22-06-1982		JP 1282819 C JP 56032506 A JP 59010724 B BE 884866 A1 BR 8005307 A CA 1138148 A1 DE 3031540 A1 FR 2463791 A1 GB 2056996 A , B IT 1193551 B NL 8004745 A , C	27-09-1985 02-04-1981 10-03-1984 16-12-1980 04-03-1981 21-12-1982 09-04-1981 27-02-1981 25-03-1981 08-07-1988 26-02-1981
US 6242548	B1	05-06-2001		AU 6044399 A CA 2372222 A1 EP 1185583 A1 WO 0069969 A1	05-12-2000 23-11-2000 13-03-2002 23-11-2000
EP 0603935	A	29-06-1994		BE 1006439 A3 AT 191724 T AU 670976 B2 AU 5249693 A BR 9305106 A CZ 9302853 A3 DE 69328345 D1 DE 69328345 T2 EP 1364971 A2 EP 0603935 A1 EP 0940411 A2 ES 2147192 T3 FI 935772 A GR 3033922 T3 HU 66491 A2	30-08-1994 15-04-2000 08-08-1996 30-06-1994 28-06-1994 13-07-1994 18-05-2000 07-12-2000 26-11-2003 29-06-1994 08-09-1999 01-09-2000 22-06-1994 30-11-2000 28-11-1994

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0603935	A	NO 934729 A	22-06-1994
		PL 301589 A1	27-06-1994
		PT 603935 T	31-10-2000
		US 6344522 B1	05-02-2002
		US 6407185 B1	18-06-2002
		US 6136924 A	24-10-2000
		ZA 9309588 A	11-08-1994